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Predictive model for migration of metallic cations in natural sediments

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Abstract

Recently, a sorption model based on ion exchange equilibria was proposed and successfully applied to predict the sorption behavior of metallic cations in natural sediments under batch conditions [1]. In the present study, this sorption model is coupled with a 1-D transport simulation code to check its validity under dynamic conditions. Therefore, reactive transport experiments of major cations (Ca, Na) using a natural sediment column were studied in the laboratory. A comparison between experimental and predicted breakthrough curves is reported. Results show that the sorption model coupled with the transport code is able to predict with good confidence the migration of major cations in a natural sediment. The participation of protons in the ion exchange process was confirmed by the variation of the experimental pH, coinciding with the model's prediction.

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1. Introduction

For many environmental purposes, it is essential to understand and predict with a good confidence the migration of metallic species in complex systems such as soil and sediment. In order to achieve that, reactive transport models including both transport and chemical processes can be used, although they must be correctly constrained as much as possible. In many environmental situations, sorption processes can be the main chemical reaction involving aqueous species and colloid/solid particles located in complex systems, such as sediments. Numerous models have been developed in the past to predict

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sorption processes on pure minerals. The main ones are based on ion exchange formalisms (e.g., Gaines-Thomas, Vanselow, Gapon) and/or surface complexation approaches [2-4].

At our knowledge, additivity of the sorption properties of pure mineral phases selected to describe sorption of a complex solid has not been proven when a classical ion exchange formalism was chosen. With the surface complexation approach, this additivity property cannot be generally applied in complex materials. This behavior is due to the difficulty of determining some of the parameters such as specific surface area or electrical fields of each different mineral constituting the complex material. In this context, some authors [3] prefer the Generalized Composite modeling approach, less chemically rigorous but more simple to incorporate in the reactive transport models. However, a multi-site ion exchanger model was recently proposed for a montmorillonite (i.e., pure swelling clay mineral) and was applied with success to describe sorption on complex materials (soil and sediment) [1,4].

The aim of this study is to couple this ion-exchange model with a 1-D transport simulation code and to check its validity in dynamic conditions. Therefore, the sorption of major cations (Ca, Na) on a natural sediment was studied by performing column experiments in the laboratory, and a comparison between experimental and predicted breakthrough curves is reported and discussed here.

2. Multi-site ion exchanger model

The ion-exchange model proposes that each mineral phase constituting a complex solid is characterized by several sorption sites (called X_i^-) able to exchange cations with the aqueous phase. For each site, the ion-exchange reaction between H^+ and a metallic cation (e.g., M^{n+}) can be described as follows:

$$n\{X_i^- H^+\} + M^{n+} \leftrightarrow \{(X_i^-)_n M\} + nH^+ \qquad \textit{Reaction 1}$$

Activity coefficients of the sorbed species are generally not known. However, by considering that the ratio between the activity coefficients of the sorbed species is equal to one, Reaction 1 can be associated to an apparent thermodynamic constant, called selectivity coefficient as defined below:

$$K_{H/M}^{i} = \frac{\{H^+\}^n \left[(X_i^-)_n M\right]}{\{M^{n+}\}\left[X_i^- H^+\right]^n} \qquad \textit{Equation 1}$$

where *i* denotes the type of the sorption site, { } is the activity of aqueous species, [ ] is the concentration of the sorbed species (mol/kg).

3. Materials and experimental methods

The raw material used for the column experiments was the Bt horizon of a natural soil taken from the site coded R-DBZ (Pierrelaye, France) (see more details in [5]). This material has a sandy clayey texture (70.7% sand, 8.9% silt, 20.4% clay according to [5]). Its Cationic Exchange Capacity (i.e., CEC) was measured by displacement of major cations by a 50 mmol/L CsCl solution at pH >9, and an average value of 12.9±0.9 meq/100g was obtained. Considering that pure Wyoming montmorillonite has a CEC equal to 89.2 meq/100g, the Bt horizon is equivalent to an exchanger phase composed of 14.5 wt% of pure Wyoming montmorillonite. The content of carbonated phases in the material was estimated at ~ 4 wt% after the decarbonatation experiment. The solid material was sieved in air dry conditions and the 250-315µm size fraction was selected for the column experiments. A glass column (Omnifit®) with a diameter

of 10 mm was then filled with ~ 4g of this material. The length of the filled column was ~ 3.5 cm, leading to a total porosity of ~ 41%. Before the water saturation step, the column was flushed using $N_2O_{(g)}$ to avoid any air bubble inside the system. The column was then saturated by circulating a 5 mmol/L $CaCl_2$ solution for a duration corresponding to the replacement of at minimum 200 Pore Volumes (PV). After this saturation step, Ca^{2+} and H^+ are the main sorbed cations on the exchanger. Influent solutions are pumped through the column using a piston pump (P500, Pharmacia®), which allows maintaining a constant flow rate from 1 to 999 mL/h. An injection valve located in the upstream of the column allows the injection of a solution different to the background solution (i.e., 5 mmol/L $CaCl_2$ solution). A pH/conductivity meter (P/C, Pharmacia®) at the outlet of the column offers online measurement of pH and conductivity. The effluent is collected by a fraction collector (Omnicoll®, Lamda) and analyzed by ion chromatography.

Different column experiments were carried out to study Ca^{2+} and H^+ displacement by Na^+. The one presented here consisted in injecting successively 4 PV of a 50 mmol/L NaCl solution, 0.8 PV of a 5 mmol/L $CaCl_2$ solution, and 4 PV of 45.7 mmol/L $CaCl_2$, before returning to the circulation of the background electrolyte (5 mmol/L $CaCl_2$). Experiments were performed in duplicate at two different flow rates (6 and 9 mL/h) and the injected solutions were in equilibrium with atmospheric $CO_{2(g)}$.

4. Experiment results

Fig. 1A shows the experimental breakthrough curves (BTC) obtained for pH and aqueous Na, Ca and Cl as a function of the number of pore volumes (PV) injected in the column. As noticed, the results are independent of the flow rate used, whatever the element analyzed.

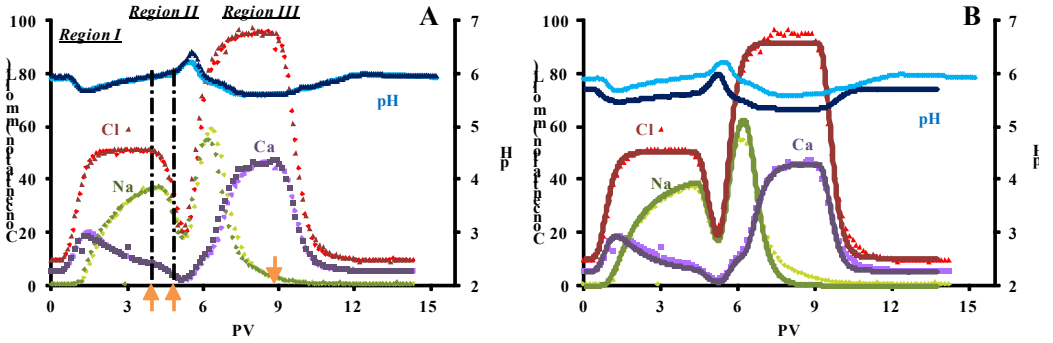

Fig.1: Breakthrough curves obtained for pH and concentrations of aqueous Na, Ca and Cl reported as a function of the number of pore volumes (PV) injected in the column. Experimental results obtained at two different flow rates are reported on Fig. 1A while Fig. 1B compares experimental results (dot symbols) obtained at a flow rate of 6 mL/h with calculated BTC (lines) predicted by our model. The arrows indicate the injection of solutions having different chemistry as detailed in the text (section 3).

The breakthrough curves can be divided into 3 regions. In the region I, corresponding to the 0-4 PV, Ca cations initially present on the exchanger phase are displaced from the sediment column by Na cations. The Ca aqueous concentration increases rapidly up to 20 mmol/L at around 1 PV and then decreases gradually. After 1 PV, the concentration of Na starts to increase from zero to a maximum of around 38 mmol/L at ~ 4 PV. The region II begins at 4 PV when the background solution is injected into the column. This leads to a decrease of the Na concentration and a peak shoulder for the Ca concentration between 4 and 4.8 PV. The region III corresponds to the injection of 4 PV of a 45.7 mmol/L $CaCl_2$ solution and the background solution was reintroduced at 9 PV. At the beginning of the region III,

aqueous concentrations of both Na and Ca are minimum. Then, these concentrations increase concomitantly as a result of the 45.7 mmol/L $CaCl_2$ injection. The Na concentration reaches a maximum around 6 PV (~ 60 mmol/L) and then decreases gradually due to the displacement by Ca cations.

In the three regions, pH evolves (see Fig. 1A). This means that despite the fact that Na and Ca are the main cations sorbed on the solid phase during the experiments, H^+ are also involved in the ion exchange reactions. Since the pH of the background solution was around 5.8, one can assume that the carbonate phases are no longer presented in the column. However, on the basis of the experimental results, the dissolution of such phases cannot be completely discarded. Modelling will help to discriminate between these different processes (ion exchange reactions involving H^+ *vs* dissolution of carbonate phases).

5. Predictive Modeling, Discussions and Perspectives

As detailed in section 3, the sediment can be considered as an exchanger phase composed of 14.5 wt% of pure Wyoming montmorillonite. Then we used the published selectivity coefficients obtained for Wyoming montmorillonite [1] to predict the sorption capacity of this complex solid. This ion exchange model was implemented in a 1D transport code (Phreeqc [6]). Two hydrodynamic parameters are required by the software: porosity and dispersivity. While the porosity was measured experimentally, the dispersivity was obtained by inverse modeling of experimental BTC of an inert tracer (Cl^-), yielding a value around 0.02 m. Modeling was performed assuming that injected solutions were in equilibrium with atmospheric $CO_{2(g)}$ and the absence of carbonate phases in the solid material. The comparison of the predicted BTC with the experimental ones are shown in Fig. 1B. Overall, the reactive transport model predicts with good confidence the experimental data obtained for both Na and Ca. Moreover, the shape of the pH curve is well reproduced by the model, despite a difference of 0.2 unit observed between calculated and measured pH. This difference could be due to a problem relating to the calibration of the pH electrode in static condition while measurements were carried out in flow-through conditions. To investigate the effects of a possible dissolution of the carbonate phases in our experiments, another modeling was carried out by adding a kinetic module of calcite dissolution in the simulation code, giving a pH variation totally at odds with the experiment results. Thus we can exclude that pH is controlled by reactions with carbonate phases during reactive transport.

The results reported in this study reveal that the pH level is controlled by $CO_{2(g)}$ solubility without any contribution of the dissolution of the carbonate phases. However, the pH variation is solely related to the ion-exchange reactions involved in the experiments. This means that the reactions depicting Na/Ca exchange on the solid cannot be described without taking into account the sorption of H^+, a competitive ion always present in natural water. Further column experiments will be performed with more reactive materials such as carbonate sediments.

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